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Method for Manufacturing Polyester Elastomer Sheeting

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Elastomer Sheeting

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(57) Claims

(1) A method for manufacturing polyester elastomer sheeting, characterized in that a crystalline polyester elastomer having a melting point of 140°C or higher is melt-molded into sheeting or an article in the form of a sheet, then calendered in the transverse direction while simultaneously being calendered in a longitudinal direction, and heat-treated.

- (2) The method for manufacturing polyester elastomer sheeting according to Claim 1, wherein the polyester elastomer is obtained from an aromatic dicarboxylic acid, an aliphatic glycol, and at least one compound selected from among an α , ω -dihydroxy aliphatic polyether having an average molecular weight of 400 to 6000, an α , ω -dihydroxy aliphatic polyester having an average molecular weight of 400 to 6000, and an aliphatic dicarboxylic acid having ten or more carbons.
- (3) The method for manufacturing polyester elastomer sheeting according to Claim 1, wherein the calendering is performed at a temperature ranging from the glass transition point of the polyester elastomer to at least 30°C below the melting point, and at a calendering ratio of seven times or lower in the longitudinal direction.
- (4) The method for manufacturing polyester elastomer sheeting according to Claim 1, wherein the temperature of the heat treatment is at least 20°C or more below the melting point of the polyester elastomer.

Detailed Description of the Invention

The present invention relates to sheeting comprising a polyester elastomer, and in particular relates to a method for manufacturing sheeting that is ideally used for belting.

So-called thermoplastic polyester elastomers synthesized from an aromatic dicarboxylic acid, an aliphatic glycol, and an α , ω -dihydroxy aliphatic polyether generally have a high melting point; exceptional chemical-resistance, flexibility and fatigue resistance; superior creep resistance as a crystalline resin, as compared to other thermoplastic elastomers having low crystallinity such as polyurethane; and other characteristics. Such characteristics are suited to belting, and attempts have been made to use individual molded polyester elastomer sheeting for light-load conveyor belting. However, the creep phenomenon will cause belting to lengthen, which is a drawback when belting made from individual sheeting as described above are subjected to high tensile loading, or are used in high-temperature environments.

A canvas or the like should be laminated to the sheeting in order to prevent the creep phenomenon from occurring, but the canvas material or the adhesive used for lamination purposes will degrade to an appreciable degree in such circumstances. For example, polyester

JP 1 - 49741 B2 Page 2

elastomers have inherently exceptional heat ageing resistance, but the performance of the bonding agent; i.e., its heat ageing resistance, flexibility, and the like, is relatively inferior. The drawback also exists that the layers separate during use, thereby not only restricting to a considerable degree the range of application for composite belting, but creating other drawbacks such as reduced durability. If the creep resistance of the individual sheeting could be dramatically enhanced, the resulting belting would theoretically be unprecedentedly simple to use, light in weight, devoid of any problems relating to loosening of the canvas or separation between the sheeting and the canvas, and endowed with exceptional hygienic properties.

Stretching individual sheeting either uniaxially or biaxially will provide the resulting sheeting with strong resistance to plastic deformation and exceptional creep resistance. Initially, the entirety of the sheeting will be elongated in a substantially uniform manner when so-called tensile stretching is performed, but a so-called "necking" phenomenon will arise, whereby localized constriction will occur when the tensile yield of the material is surpassed, leading to elongation. Accordingly, a draw ratio of approximately five to eight times is normally required to ensure that the entire sheeting is uniformly stretched. For example, when 1-mm-thick sheeting needs to be obtained as an end product, uniaxial stretching will accordingly require the original sheeting to be approximately 5 mm thick, and biaxial stretching will require an even greater thickness. Strong forces and powerful equipment are required to prepare and then stretch sheets of such thickness and width, which not only presents numerous obstacles to practical application, but also provides absolutely no economic benefit.

Further operational drawbacks are also created; for example, if the original pre-stretched sheeting is to be pre-heated, then heating it over a short period of time will prove problematic if the sheeting is of an appreciable thickness. Another major drawback arises in uniaxially tensile-stretched sheeting, which is highly likely to tear along the longitudinal direction.

The present inventors conducted diligent research into a method for manufacturing sheeting with which stretching-related effects could be obtained, but without any occurrence of the "necking" phenomenon. As a result, the inventors entirely unexpectedly arrived at the method of the present invention by means of successfully obtaining the stretching-related effects without any occurrence of the "necking" phenomenon through the use of rolls to flatten a polyester

JP 1 ~ 49741 B2 Page 3

elastomer in a lengthwise direction, while simultaneously flattening the elastomer to a certain degree in the transverse direction; i.e., by means of calendering the elastomer. Specifically, the present invention is characterized in that a crystalline polyester elastomer having a melting point of 140°C or higher is melt-molded into sheeting or an article in the form of a sheet, then calendered simultaneously in the transverse direction and a longitudinal direction, and heat-treated.

According to the present invention, the entirety of the sheeting may be evenly flattened to a sufficient degree without any occurrence of the "necking" phenomenon, even at a calendering ratio of approximately two to three times. Furthermore, the strength may be increased to a level commensurate with sheeting that has been stretched and elongated about 500–800%; the likelihood of tearing along the longitudinal direction is considerably lower than with uniaxially stretched sheeting; and sheeting having exceptional tear strength may be obtained.

The stretching effect attributed to calendering had never been obtained before the crystalline polyester elastomer with a high melting point was calendered in the invention of the present specification, and virtually no effect has even been observed when thermoplastic polyurethane elastomers are calendered to improve their creep resistance. In addition, it has been impossible to obtain the anticipated enhancing effect polyester elastomers, even if polymers that have low crystallinity and a melting point of 140°C or higher are calendered. The exceptional effects of the polyester elastomer of the present invention are believed to be attributable to its high melting point, high crystallinity, and definite tensile yield point.

Examples of the polyester elastomer used in the present invention include polyester-polyether block copolymers in which polyethylene terephthalate, polypropylene terephthalate, polybutylene terephthalate, polyethylene terephthalate-isonaphthalate, polyethylene terephthalate-butylene terephthalate, or another aromatic polyester is used as the hard segment, and polyethylene ether glycol, polybutylene ether glycol, polyethylene ether glycol, polyethylene ether glycol-polybutylene ether glycol, or another α , ω -dihydroxy aliphatic polyether is used as the soft segment; polyester-polyester block copolymers in which an aromatic polyester mentioned above is used as the hard segment, and polyethylene adipate, polyethylene sebacate, polybutylene adipate, polyethylene adipate, polyethylene adipate, polyethylene, or another α , ω -dihydroxy

IP 1 - 49741 B2 Page 4

aliphatic polyester is used as the soft segment; and random copolymers formed from terephthalic acid, isophthalic acid, or another aromatic dicarboxylic acid; adipic acid, sebacic acid, azelaic acid, dimeric acid, w-caprolactone, or another aliphatic carboxylic acid; or ethylene glycol, propylene glycol, butylene glycol, neopentyl glycol, cyclohexane dimethanol, or another diol. The aforementioned α, ω -dihydroxy aliphatic polyether and α, ω -dihydroxy aliphatic polyester typically have an average molecular weight of 400 to 6000, and preferably 800 to 3000. Two or more of the aforementioned polyester elastomers may be blended together, while polyester elastomers comprising two or more different soft segments; e.g., a polyether and polyester in combination, may also be used. Other materials that may be used include copolymers containing a small amount of trimellitic acid, glycerine, or another branching component, and elastomers whose terminal carboxyl groups are blocked by an epoxy compound or the like. Of particular preference are polyester elastomers obtained from an aromatic dicarboxylic [acid], an aliphatic glycol, and at least one compound selected from among an α,ω -dihydroxy aliphatic polyether having an average molecular weight of 400 to 6000, an α, ω -dihydroxy aliphatic polyester having an average molecular weight of 400 to 6000, and an aliphatic dicarboxylic acid having ten or more carbons. The polyester elastomer must be crystalline, and have a melting point of 140°C or higher, and especially preferably a melting point of 160°C of higher.

The proportion of the soft segment is preferably approximately 10 to 80 wt%, although the composition may dictate otherwise. An additive such as an organic or inorganic filler, nucleating agent, stabilizer, conductive agent, flame retardant, colorant, or lubricant may be compounded with the polyester elastomer as required by the application, provided that the inherent physical characteristics thereof are not adversely affected. It is preferable for no additive, or just the minimal amount required, to be added in applications such as a conveyor belt or where direct contact can otherwise be made with foodstuffs.

The polyester elastomer is ordinarily molded into sheeting or an article in the form of a sheet by means of melt-extrusion, whereupon the sheeting or article in the form of a sheet is calendered using pressure rolls, with a typical calendering ratio preferably being two to seven times in the longitudinal direction, and one to two times in the transverse (width) direction. A

JP 1 – 49741 B2 Page 5

calendering ratio of seven times or more in the longitudinal direction will result in severe tearing (longitudinal tearing), which is a drawback. Considerations of rollability dictate that the temperature of the sheeting or article in the form of a sheet during calendering should normally range from the glass transition point of the polyester elastomer to at least 30°C below the melting point, and preferably from normal temperature to a temperature at least 50°C below the melting point. The thickness of the sheeting or article in the form of a sheet before being calendered preferably allows the sheeting to be molded to a thickness of approximately 0.1 to 10 mm after having been calendered.

It is essential for the calendered sheeting to be subjected to a heat-treatment, in order to prevent any dimensional variation or reduction in performance when the sheeting is used in high-temperature environments. The heat treatment is preferably performed at a temperature higher than presumably encountered by the sheeting in its environment of application, but if the temperature is too close to the melting point, the effects of calendering will be diminished by means of the heat treatment. The temperature is therefore stipulated as being at least 10°C or more, and preferably 20°C or more, below the melting point.

The heat treatment is ordinarily performed at a fixed length, although heat setting may also be performed while contraction is allowed to occur to a certain degree. Such actions are able to change the Md (modulus of elasticity) of the final sheeting.

The present invention is described below with reference to working examples.

Working Examples

Sheeting (thickness: 3 mm; width: 500 mm) comprising polyester polyether elastomer synthesized from terephthalic acid, 1,4-butanediol, and a polytetramethylene ether glycol with an average molecular weight of 1000 (melting point: 200°C; polytetramethylene ether glycol content: 40%; intrinsic viscosity: 0.9 (measured at 30°C in phenol/tetrachloroethane in a weight ratio of 3/2)) was extrusion molded by means of a common method. The temperature during extrusion molding was 220°C, and the temperature of the chilled roll was 50°C.

JP I – 49741 B2 Page 6

^{* [}Translator's note: in Claim 3, it is specified that the calendering ratio should be seven times or less, which contradicts the range of seven times or more specified here.]

The sheet was calendered under the conditions described hereunder, and thereafter subjected to a heat treatment. The sheeting was passed through and heated in a preheating chamber that had been set to 80°C, and then calendered 2.5 times in the longitudinal direction while being calendered 1.2 times in the transverse direction, between pressure rolls that had been heated to 100°C. The ratio in the longitudinal direction was adjusted according to the ratio of rate of rotation of the reduction and take-up rolls, while the ratio in the width-wise direction was adjusted according to the pressure applied by the pressure rolls. The calendered sheet was heat-set as a result of being passed at constant length though a 160°C heating chamber connected to the take-up roll. The sheeting traveled at a rate of 15 m/min, and the heat setting lasted two minutes. The physical characteristics of the resulting calendered, heat-treated sheeting were evaluated, and are shown in Table 1. For purposes of comparison, extruded unstretched sheeting was uniaxially stretched 500% at 100°C and heat-set at 160°C. Its physical characteristics are also shown in Table 1.

Table 1

| | | Uncalendered sheeting | Calendered sheeting (of the present invention) | Stretched sheeting (comparative example) |
|--|-----------------------|--------------------------|---|--|
| Tensile strength | (kg/cm ²) | 310 | 1150 | 1230 |
| Tensile elongation | (%) | 600 | 110 | 90 |
| Modulus of elongation | (kg/cm ²) | 1100 | 1050 | 1150 |
| Tear strength (longitudinal direction) | (kg/cm ²) | 120 | 55 | 8 |

The superiority of the calendering method of the present invention is clearly evident from the longitudinal tear resistance.

Fig. 1 shows the stress-elongation (S-S) curves of calendered and heat-treated sheeting; Fig. 2 shows the temperature dependency of the S-S curves; and Fig. 3 shows the creep resistance (tensile creep at 100°C).

The calendering and heat treatments provided considerable strength, the change in Md with respect to temperature was dramatically improved, and creep resistance was substantially

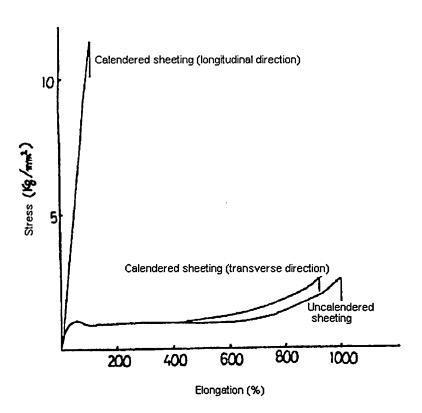
JP 1 - 49741 B2

enhanced, all of which demonstrated that the sheeting had exceptional physical characteristics. The results revealed that the sheeting could find favourable application as belting.

Brief Description of the Drawings

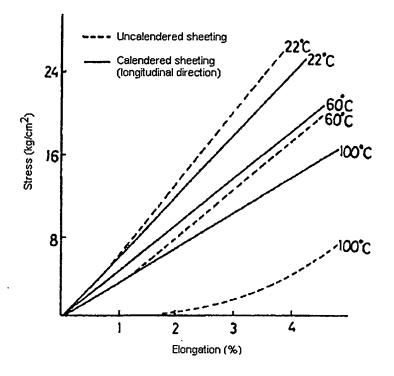
Fig. 1 is a graph depicting examples of S-S curves for calendered and uncalendered sheeting. Fig. 2 shows the temperature dependency of the S-S curves. Fig. 3 is a graph showing the creep resistance (tensile creep at 100°C).





JP 1 - 49741 B2 Page 8

[Figure 2]



[Figure 3]

